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Measurements of Liquid Methanol Content in Black Liquors

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Measurements of Liquid Methanol Content in Black Liquors

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ABSTRACT

This study demonstrated the validity of the integrated buffer solution method with gas chromatography analysis for the measurements of liquid methanol content in Kraft mill black liquor samples. The measurements of four black liquor samples from two mills indicated that liquid methanol content in weak black liquor from a brownstock washing stage is about 4000-6000 ppmm of liquor solids. The measurements also indicated that softwood liquors have a slightly lower concentration of liquid methanol than that of hardwood liquor samples.

INTRODUCTION

With the increasingly restrictive environmental regulations, maintaining environmentally sound and technologically competitive operations in pulp and paper mills is a key to the success of the U.S. pulp and paper industry. The new toxic and permit provisions of the 1990 amendments to air emission regulations require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. Many VOC's are now designated as hazardous air pollutants (HAP's). The release of VOC's during mill operations is determined by several factors: (1) the liquid VOC content in mill streams, (2) the fundamental thermodynamic phase equilibrium behavior of the VOC's in mill streams, (3) the mass transfer associated with specific mill processes, and (4) the mill operating conditions, such as wood species, pulping chemicals used, water reuse in operation, etc. Because several factors pertain to unit operating conditions and specific mill processes, such as mass transfer in a unit operation, it is very difficult to generalize for all the specific situations. However, the liquid VOC content in the mill liquid streams is a key factor that controls the VOC release in mill operations. Therefore, it is important to be able to measure liquid VOC content in mill streams for VOC release predictions.

Recently, NCASI conducted a series of studies at several Kraft mills to characterize the emissions of volatile HAP's and VOC's from chemical pulp mills in 1993 and 1994. The results of the studies were published in a series of nine NCASI Technical Bulletins (NCASI, 1994). The results as summarized by Jain (1996a) showed: (1) paper machines, brownstock washers, oxygen delignification systems, smelt dissolving tanks, and bleach plants were the major contributors to VOC emissions from Kraft mills; (2) methanol constituted the major fraction (about 90%) of HAP's from most sources; and (3) water reuse practice will significantly contribute to the VOC emissions in Kraft mills. NCASI's study indicated that the characterization of liquid methanol content in weak black liquor is an important task in understanding VOC release in pulp and paper mills.

Unfortunately, limited methods are available to measure liquid methanol in black liquors due to the corrosive nature of black liquors. Gunshefski and Cloutier (1994) suggested using a buffer solution to precipitate the solids in black liquor followed by direct measurement of liquid methanol in the buffered solution using gas chromatography. However, no conclusive study was reported about the method. The objectives of the present research are to: (1) demonstrate the buffer solution method for the measurement of liquid methanol content in black liquor, (2) integrate the buffer solution method with the direct injection gas chromatography analysis for characterizing liquid methanol content in weak black liquor, and (3) obtain liquid methanol data in Kraft black liquor samples.

EXPERIMENTAL

The Buffer Solution Method

Black liquor contains dissolved organic and inorganic materials. The dissolved solids (DS) content of the four samples used in this study is about 15%. DS in the black liquor would deposit into the column of a gas chromatograph (GC) if mill black liquor is analyzed by a GC using direct injection. Any solids trapped in the column can inhibit the transportation of the vaporized compounds through the column and cause measurement errors. The buffer solution method developed by Gunshefski and Cloutier (1994) is designed to precipitate the solid in the liquor samples prior to direct GC analysis.

In this study, the buffer solution was comprised of potassium hydroxide (KOH), potassium phosphate (K_2PO_4), and nanopure water (H_2O). To make the solution, 20g of KOH and 68g of K_2PO_4 were added to one liter of nanopure water. The buffer solution was then added to black liquor samples to precipitate the solids. The mass ratio of buffer solution to black liquor was 30:1. After the buffer solution was added, the samples were refrigerated for about 24 hours until all the solids were precipitated out. Once the solids were precipitated out, they were easily distinguishable from the liquid with the naked eye. It was found that the pH of the buffer solution changed from highly alkaline to about 7 after adding black liquor, indicating a chemical reaction between the solids and the alkaline buffer solution. It is hypothesized that these reactions do not affect the methanol content as indirectly verified in this study.

Black Liquor Samples

In this study, four black liquor samples were obtained from two separate Kraft mills (Mill A and Mill B). Each mill provided one softwood and one hardwood black liquor sample.

Direct Injection GC Calibration

GC measurement is a relative measurement. Calibration is required to obtain the absolute mass of a measured compound. In this study, calibration of methanol was conducted using mixtures of methanol with nanopure water at several mixing ratios. Calibration was performed using concentrations of methanol from 2 to 30 ppmv in increments of 2 ppmv. A HP 5890A GC was used for all measurements. The calibration curve is shown in Fig. 1, where the vertical coordinate is the part-per-million of methanol by mass (ppmm) and the horizontal coordinate is the integrated GC peak area output on the strip chart.

GC Measurements of Methanol in Black Liquor Samples

Methanol content in the black liquor can change due mainly to evaporation and phase partitioning within the liquid as temperature varies in mill streams. NCASI found that temperature contributed to inconsistencies in its laboratory measurements (Jain, 1996b). An experimental apparatus capable of varying sample temperature was constructed to study the effect of temperature on the measured methanol content. Fig. 2 illustrates the apparatus setup.

During the experiments, both the hardwood and softwood black liquor samples from the two mills were heated from 25 to 95 °C in increments of 10 °C, and then heated to 100 °C. The GC injection sample size was 10 μL. The data were recorded at each of these temperatures. Three duplicates were made and averaged for each temperature. It was found that methanol was present in all of the samples.

There are limited methods available to measure the liquid methanol content in black liquors. The verification of the integrated buffer solution method with GC analysis is difficult. In this study, an indirect method was used to assure the validity of the buffer solution/precipitated solids method. Known amounts of additional methanol were incrementally added to the Mill A buffered softwood liquor to a final estimated value of 47 ppmv of methanol to buffered liquor, which is about two times the initial methanol concentration to avoid a large measurement error. The measured difference in methanol content before and after addition was compared with the known amount added.

DATA ANALYSIS AND RESULTS DISCUSSION

Results

The results are reported as mass methanol per mass of dissolved solids in black liquor to make meaningful comparisons of the liquid methanol content in different liquor samples.

Solids Content of Black Liquor Samples

The solids content of the samples was measured before the GC analysis using TAPPI method T650 om-89. Three duplicate measurements were made for each sample. The results are listed in Table I.

GC Analysis Results of the Black Liquor Samples (Direct Injection)

Table II lists the results of the measurements using the calibration curve shown in Fig. 1. The maximum measurement uncertainty was about 3 ppmm calculated from the three duplicate measurements for each test. The data show a general trend that the liquid methanol concentration within the buffered solution decreases as temperature increases. This is probably due to the evaporation of methanol at high temperatures.

As discussed, the methanol content measurements were indirectly verified by incrementally adding known amounts of methanol to the buffered black liquor. The methanol concentration was calculated before and after each addition. The measured methanol concentration was consistent with the calculated data (the original methanol plus the known amount of methanol added) for the liquor as shown in Fig. 3. The maximum discrepancy between the measured and calculated methanol content is less than 3 ppmv, within the measurement accuracy of the current experimental system. The verification measurements demonstrate that the presence of the buffer solution does not change the original methanol content in the black liquor samples. Therefore, the integrated buffer solution method with GC analysis for liquid methanol content measurements in weak black liquors is valid.

GC Data Comparison and Discussion

The comparison between the hardwood and softwood data is plotted in Figs. 4 and 5, respectively. The comparison between the data from Mill A and Mill B is plotted in Figs. 6 and 7, respectively. The maximum measurement uncertainty is about 8%, which is mainly due to the low methanol concentration in the buffer solution (~30 ppmv). The actual measurement error is less than 3 ppmv.

It can be seen from the figures shown that the liquid methanol in these four liquor samples is about 4000-6000 ppm of solid mass. As temperature increased, methanol concentration decreased due to evaporation. The methanol concentration decreased sharply when temperature reached about 85°C. This behavior is more prominent for hardwood as shown in Fig. 4. However, significant methanol evaporation was not observed at the methanol boiling temperature of 65°C. There is a consistent dip on the curve at temperature 45°C as shown in Figs 4,5,6,7. At this time, we do not know whether it is due to systematic measurement errors or some actual physical phenomena. We will verify this in the future experiments.

The results also show that the liquid methanol content in Mill A liquor samples are consistently lower than that found in Mill B liquors. The liquid methanol content in the hardwood black liquor samples between Mill A and Mill B is about 20% based on solid mass basis as shown in Fig. 4. The difference in the softwood black liquor samples between Mill A and Mill B is also about 20% as shown in Fig. 5. The differences indicated the variability of the methanol content in black liquors from mill to mill. Therefore, VOC release will depend on specific mill operations.

The wood species also appears to be a major factor affecting the liquid methanol content in black liquors. The liquid methanol contents in hardwood liquors are consistently higher (about 20%) than those in softwood liquors for all the liquors from both Mill A and Mill B as shown in Figs. 7 and 8. The difference may be due to the higher methoxyl content of hardwood lignin than that of softwood. On the other hand, the hardwood and softwood are usually cooked to different kappa numbers during their respective pulping processes, and the reactivities of the methoxyl groups in hardwood and in softwood structures will also differ. All these factors could contribute to the difference in the measured methanol content in hardwood and softwood black liquors (Sonnenberg and Ragauskas, 1996). However, the data obtained suggest that wood species is an important factor controling the methanol content in black liquor. This, in turn, will affect the release of VOC's into the air in mill operations.

SUMMARY AND CONCLUSIONS

- The results showed that the typical methanol content in the four mill weak black liquor samples was about 4000-6000 ppm mass solids.
- The methanol contents measured in the hardwood black liquors were somewhat greater than those measured in the softwood black liquors possibly due to the differences in wood molecular structures, indicating that wood species can affect the release of VOC's in mill operations.
- Furthermore, the methanol contents of the Mill B liquors were somewhat lower than those of the Mill A liquors, indicating the variability of the methanol content in mill streams.

- The indirect verification of the measurements indicated that the integrated buffer solution method with GC analysis can provide reliable measurements of the liquor methanol in black liquor samples.
- Further studies on vapor phase methanol concentrations are necessary to obtain the thermodynamic data required for more precise prediction of the release of VOC's into the air.

ACKNOWLEDGMENTS

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Sonnenberg, L. B. and Ragauskas, A. J., (1996), Private Communication. Institute of Paper Science and Technology, Atlanta, GA.

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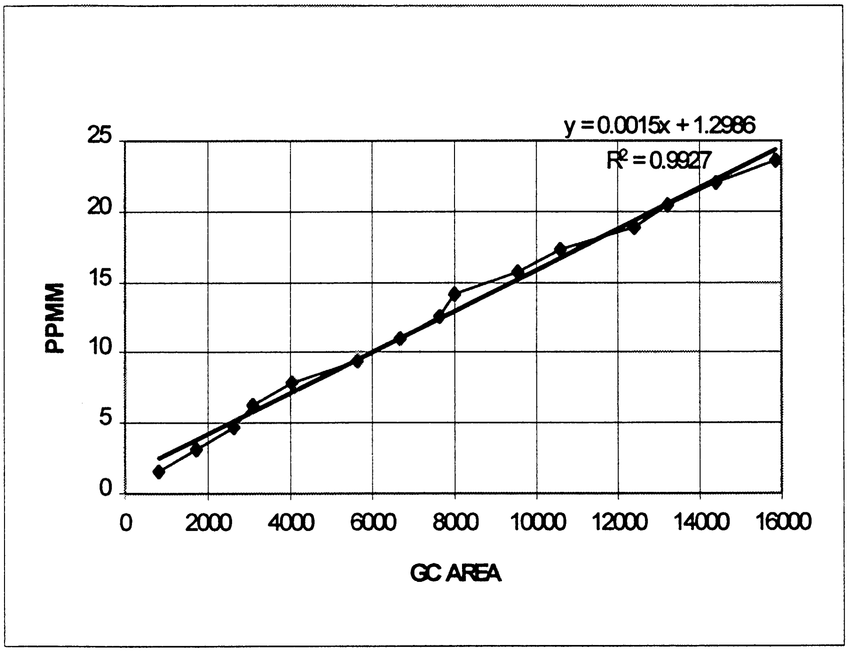

y = 0.0015x + 1.2986
R² = 0.9927
PPMM
GC AREA
0
5
10
15
20
25
0
2000
4000
6000
8000
10000
12000
14000
16000

Fig. 1

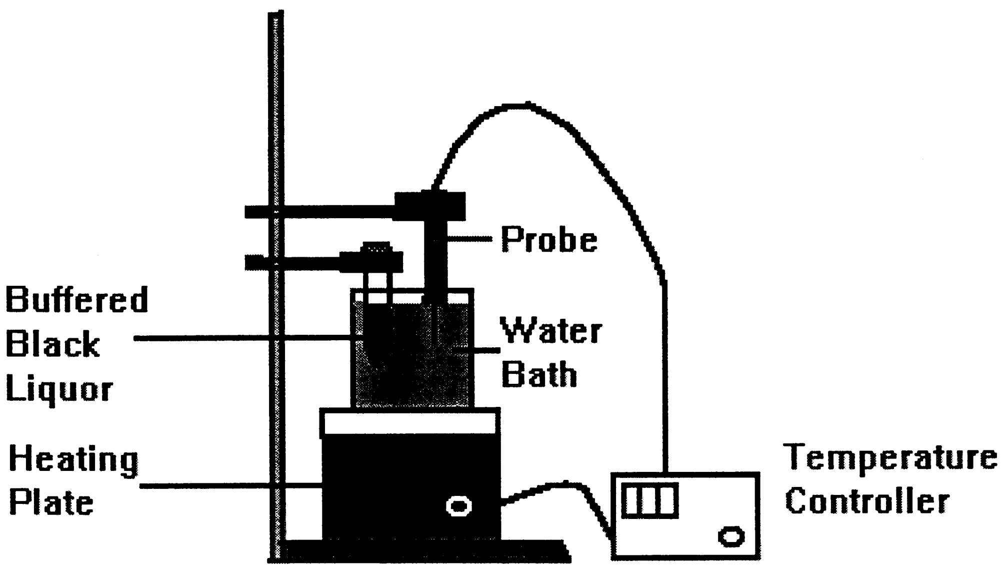
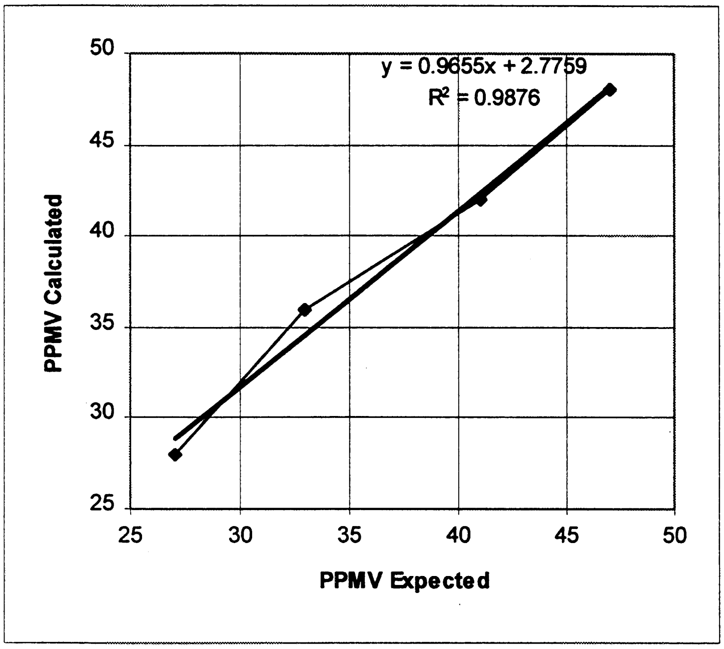

Probe
Buffered
Black
Liquor
Water
Bath
Heating
Plate
Temperature
Controller

Fig. 2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R^2 = 0.9876
PPMV Calculated
PPMV Expected
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40
35
30
25
25
30
35
40
45
50

Fig. 3

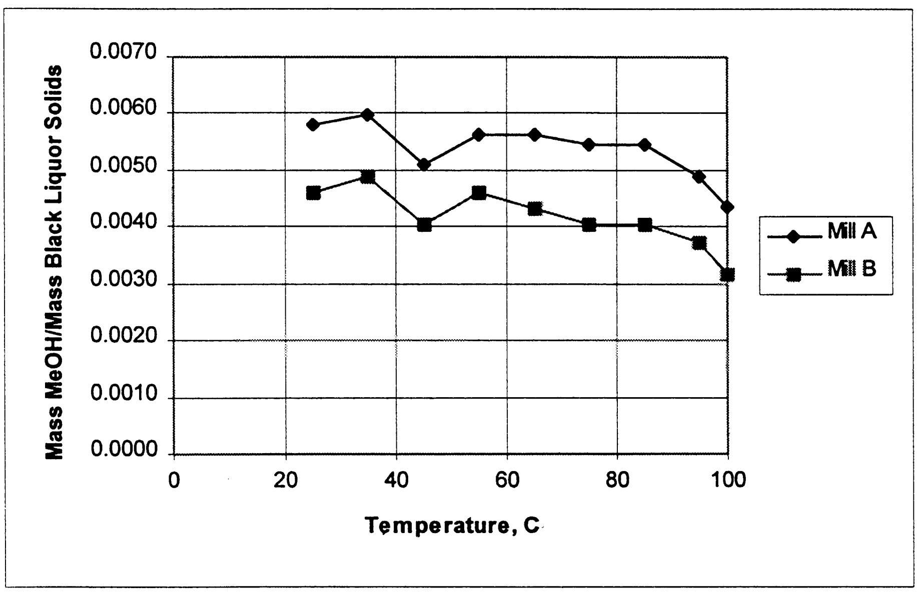
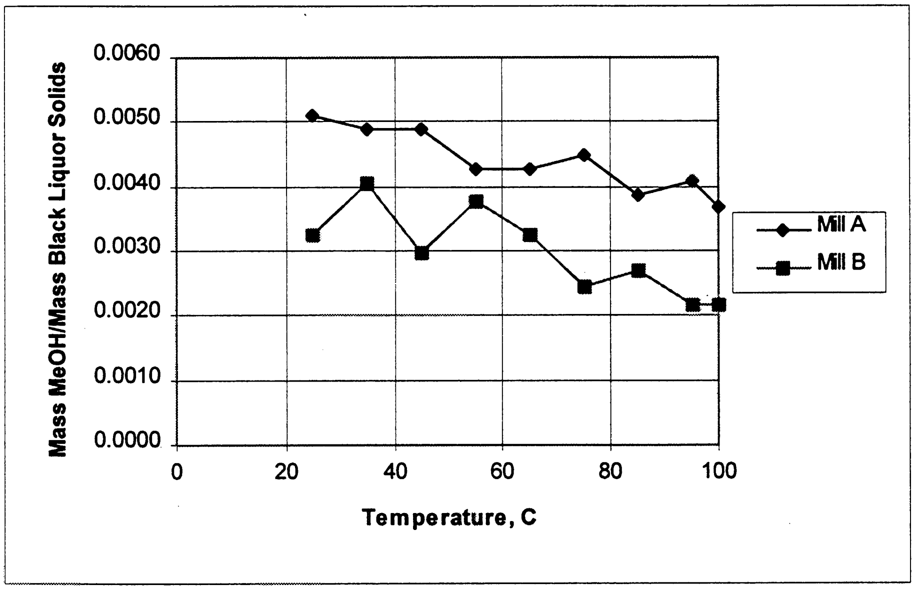

Mass MeOH/Mass Black Liquor Solids
Temperature, C
0.0070
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
20
40
60
80
100
Mill A
Mill B

Fig. 4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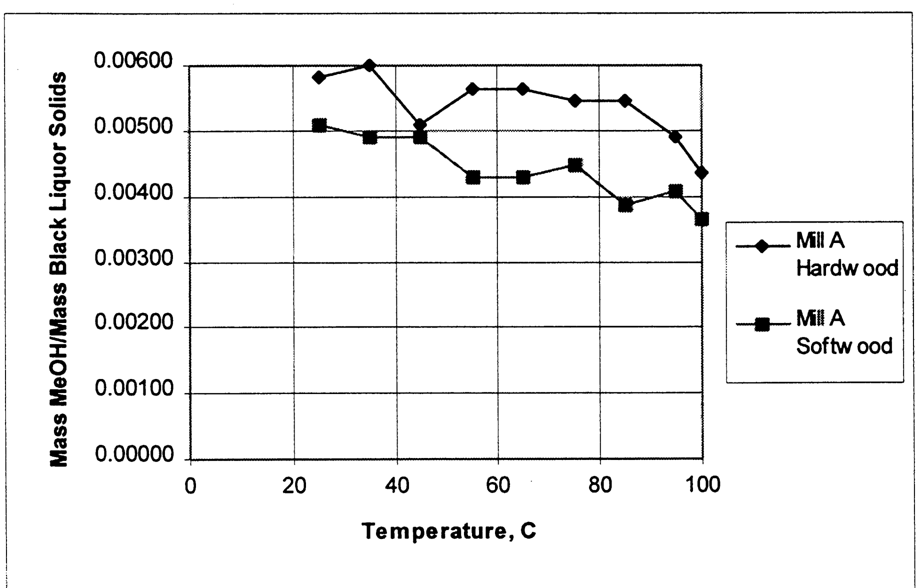
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
0
20
40
60
80
100
Temperature, C
Mill A
Mill B

Fig. 5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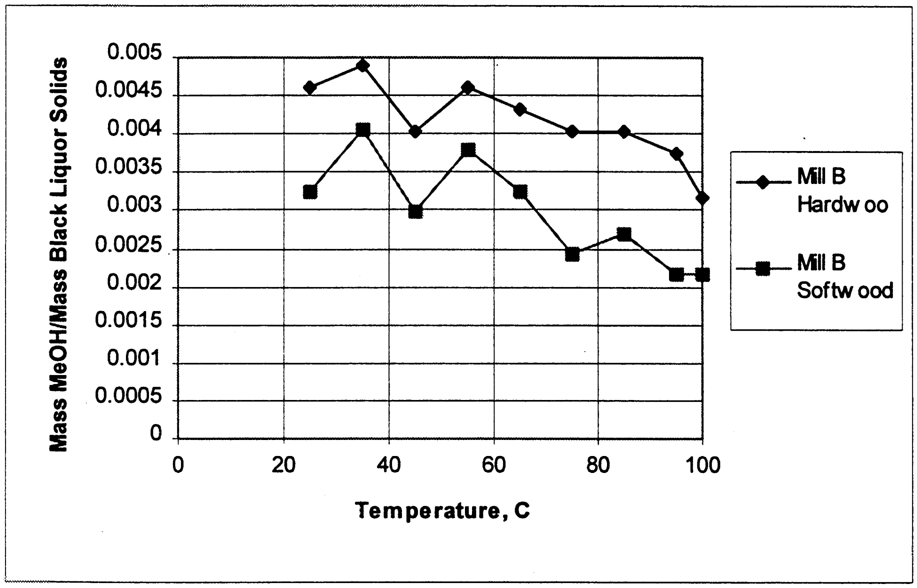
60
80
100
Temperature, C
Mill A Hardwood
Mill A Softwood

Fig. 6



Mass MeOH/Mass Black Liquor Solids
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0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0
20
40
60
80
100
Temperature, C
Mill B Hardw oo
Mill B Softw ood

Fig. 7

List of Tables

Table I. Black liquor solids measurement results.

Sample	Solids (%) Mean Value	Standard Deviation Solids (%)
Mill A Softwood	15.21	0.024
Mill A Hardwood	17.06	0.016
Mill B Softwood	11.47	0.000
Mill B Hardwood	10.76	0.033

Table II. Measured liquid methanol mass per mass of buffered solution.

Temperature (^oC)	Mill A Hardwood (ppm)	Mill B Hardwood (ppm)	Mill A Softwood (ppm)	Mill B Softwood (ppm)
25	32	16	25	12
35	33	17	24	15
45	28	14	24	11
55	31	16	21	14
65	31	15	21	12
75	30	14	22	9
85	30	14	19	10
95	27	13	20	8
100	24	11	18	8